Analysis of Centrifugal Distortion Effects in the Rotational Spectrum of Formyl Fluoride

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The measurements of the ground state spectra of both HCOF and DCOF have been extended to high-J transition. The centrifugal distortion analysis clearly showed that in HCOF the inclusion of sextic terms is absolutely necessary, whereas the effects from this source in DCOF are smaller but not negligible. The planarity condition for the sextic terms was introduced to reduce the number of parameters. Spectra in the lowest vibrational state of both HCOF and DCOF were also treated.

Introduction

As the simplest representative of the acyl fluorides, formyl fluoride has been the subject of a number of investigations by conventional microwave spectroscopy [1–3]. More recently it has been studied by laser-microwave double resonance [4] and has been shown to function efficiently as an FIR-laser [5]. It was these latter investigations which prompted interest in determining parameters which would enable high-J rotational transitions of formyl fluoride to be calculated precisely. Although millimeter-wave measurements were carried out by Favero et al. [2], the transitions measured displayed relatively small shifts due to centrifugal distortion (maximum shift $\cong$ 40 MHz). At the time these experiments were carried out the theory of centrifugal distortion had not been completely clarified and these authors derived seven distortion parameters from their results. It has, of course, been shown by Watson [6] that at the quartic level only five such parameters are necessary. Reanalysis of the available data was carried out but proved to be unsatisfactory for our purposes. In particular, several obvious discrepancies were found to be present in the data for normal formyl fluoride (HCOF). At this point it was decided to extend the measurements to higher J-values and to remeasure some of the published frequencies.

Observations

Measurements were carried out at room temperature in a conventional 33 kHz modulated Stark spectrometer on samples of both normal and deuterated formyl fluoride which were prepared according to Morgan et al. [7]. Owing to the large rotational constants of both forms of formyl fluoride, the spectra were very sparsely populated and little difficulty was experienced in extending the ground state measurements up to $J = 44$ for HCOF and $J = 38$ for DCOF. The lowest frequency vibrational mode of formyl fluoride, the FCO bending mode (ν_5), was observed [7] near 660 cm^{-1} for both HCOF and DCOF. Despite this relatively high frequency the spectra were intense enough to allow the rotational spectra of the first excited state of this mode to be observed and assigned without difficulty for both isotopic species. The frequencies measured for HCOF in the ground state and $v_5 = 1$ are shown in Tables 1 and 2, respectively. In order to avoid confusion the entire ground state data set is given in Table 1 since several of the literature values were either corrected or omitted because of apparent mismeasurement. The frequencies obtained for DCOF have appeared elsewhere [4].

Fitting the Data

The substitution of a deuterium atom in formyl fluoride has a drastic effect on the A rotational constant, reducing it from 91 GHz to 65 GHz. The centrifugal distortion effects are also considerably changed by the substitution. In HCOF the maximum centrifugal correction necessary for the transitions measured was about 4 GHz, whereas in DCOF the maximum was approximately 2.5 GHz. In DCOF a reasonable good fit was achieved with the inclusion

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Table 1. Transition frequencies of the ground state of HCOF (in MHz).

J	k_{-1}	$k_{+1} - J$	k_{-1}	k_{+1}	Frequency	c–o	J	k_{-1}	$k_{+1} - J$	k_{-1}	k_{+1}	Frequency	c–o
1	0	1 – 0	0	0	22 156.80	0.07	16	3	13 – 17	2	16	43 342.49	0.10
1	1	1 – 0	0	0	101 550.36	– 0.07	17	2	15 – 16	3	14	18 215.40	0.02
1	1	1 – 2	0	2	35 097.50	– 0.19	17	2	15 – 18	1	18	22 635.73	0.05
2	0	2 – 1	0	1	44 296.00	0.10	18	2	16 – 17	3	15	48 910.78	– 0.02
2	1	1 – 1	1	0	45 677.16	0.11	20	2	18 – 21	1	21	41 473.40	– 0.05
2	1	2 – 1	0	1	12 234.95	0.06	21	4	18 – 22	3	19	48 408.16	0.00
2	1	2 – 1	1	1	42 950.70	– 0.10	22	2	21 – 21	3	18	28 661.36	– 0.09
2	1	2 – 3	0	3	11 647.90	– 0.06	22	4	18 – 23	3	21	50 244.44	0.11
3	1	3 – 2	0	2	142 462.44	0.07	22	4	19 – 23	3	20	20 718.78	– 0.02
4	1	4 – 3	0	3	161 927.56	0.12	23	2	22 – 22	3	19	38 743.95	0.04
4	2	3 – 5	1	4	119 298.55	0.11	23	4	19 – 24	3	22	29 423.68	– 0.03
5	0	5 – 4	1	4	36 965.00	0.04	24	3	21 – 24	3	22	35 360.89	– 0.05
5	1	4 – 5	0	5	90 786.64	– 0.34	25	3	22 – 25	3	23	43 838.95	– 0.03
5	2	4 – 6	1	5	93 164.04	0.00	25	3	22 – 24	4	21	37 442.72	0.02
6	1	5 – 6	0	6	95 339.16	– 0.12	27	3	25 – 26	4	22	29 724.98	0.05
6	1	5 – 6	1	6	28 613.90	– 0.28	28	3	26 – 27	4	23	47 989.88	0.10
7	0	7 – 6	0	6	154 120.02	– 0.05	29	5	25 – 30	4	26	29 054.26	– 0.04
7	1	6 – 6	1	5	159 618.91	– 0.07	30	5	25 – 31	4	28	21 704.47	– 0.08
7	1	6 – 7	0	7	100 838.05	– 0.14	31	2	30 – 30	3	27	46 593.52	0.03
7	1	6 – 7	1	7	38 135.25	0.03	32	2	31 – 31	3	28	37 516.55	– 0.04
7	2	6 – 6	2	5	154 955.55	0.16	32	4	28 – 31	5	27	25 407.03	0.04
7	3	4 – 6	3	3	155 251.93	– 0.23	33	2	32 – 32	3	29	26 203.80	– 0.02
7	3	5 – 6	3	4	155 234.17	0.07	33	4	30 – 32	5	27	22 895.71	– 0.03
7	4	3 – 6	4	2	155 195.15	0.09	34	4	31 – 33	5	28	44 752.80	– 0.15
7	5	2 – 6	5	1	155 183.56	– 0.07	35	3	32 – 36	2	35	20 466.46	– 0.14
7	6	1 – 6	6	0	155 186.37	0.05	36	3	33 – 37	2	36	39 961.79	0.10
7	2	6 – 8	1	7	39 039.31	– 0.04	36	6	30 – 37	5	33	41 993.84	0.04
8	1	7 – 8	1	8	49 000.73	– 0.06	36	6	31 – 37	5	32	34 756.84	0.08
9	0	9 – 8	1	8	138 988.38	0.07	37	6	31 – 38	5	34	18 462.60	– 0.12
14	2	12 – 15	1	15	22 965.55	0.05	40	5	35 – 39	6	34	43 546.28	0.02
15	2	13 – 15	2	14	36 412.72	0.00	40	5	36 – 39	6	33	28 498.65	– 0.01
15	2	13 – 16	1	16	20 741.16	0.09	43	7	36 – 44	6	39	41 932.46	– 0.02
16	2	14 – 16	2	15	46 959.85	– 0.01	43	7	37 – 44	6	38	38 695.80	0.02
16	2	14 – 17	1	17	20 620.75	– 0.01							

The millimeter-wave measurements are from Ref. [2], some of the low-J transition frequencies are from Reference [3].

Table 2. Transition frequencies of $v_5 = 1$ of HCOF (in MHz).

J	k_{-1}	$k_{+1} - J$	k_{-1}	k_{+1}	Frequency	c–o	J	k_{-1}	$k_{+1} - J$	k_{-1}	k_{+1}	Frequency	c–o
2	0	2 – 1	0	1	44 207.28	– 0.25	14	2	12 – 15	1	15	27 387.76	– 0.12
2	1	1 – 1	1	0	45 606.57	– 0.24	14	3	12 – 15	2	13	44 281.59	0.65
2	1	2 – 1	1	1	42 844.39	– 0.31	18	2	16 – 17	3	15	45 352.05	0.68
1	1	1 – 2	0	2	35 891.04	– 0.07	19	2	17 – 20	1	20	39 442.65	– 0.33
5	0	5 – 4	1	4	36 100.18	– 0.26	20	2	18 – 21	1	21	48 299.55	0.28
7	2	6 – 8	1	7	41 223.03	0.51	22	4	19 – 23	3	20	26 140.22	– 0.33
11	1	10 – 10	2	9	44 394.24	– 0.27	23	4	19 – 24	3	22	35 528.49	– 0.09
11	2	9 – 12	1	12	45 191.55	0.09	29	5	25 – 30	4	26	36 220.85	– 0.33
12	2	10 – 13	1	13	37 327.30	0.06	33	4	29 – 32	5	28	46 870.64	– 0.18
							36	6	31 – 37	5	32	43 635.58	0.15

of only quartic terms [4] whereas for HCOF the necessity of sextic terms was obvious.

The inclusion of the seven sextic terms raises the number of parameters to be fitted to 15, and even with the 67 transitions available for HCOF it was difficult to determine all these constants. Formyl floride is a planar molecule and the number of independent parameters can be reduced to 14 by applying the planarity condition for a prolate rotor [8] which in Watson's S-reduction (I^r-representation) is

$$\begin{aligned}6\,C\,H_J - (B-C)\,H_{JK} - 2\,(2\,A+B+3\,C)\,h_1 \\ +4\,(4\,A+B-2\,C)\,h_2 - 6\,(6\,A+B-5\,C)\,h_3 \\ = -4\,(D_J + 2\,d_1 - 2\,d_2)^2 \\ -4\,(D_{JK} - 2\,d_1 + 4\,d_2)\,(d_1 - 4\,d_2)\,.\end{aligned}$$

The fitting of the 67 transitions of Table 1 with 14 parameters instead of the usual 15, reduced the number of correlation coefficients with values greater than 0.9 from 16 to only 5. Also the determinant of the system of normal equations – though still rather small – was increased by 4 orders of magnitude. The standard deviation achieved was 0.13 MHz and the values obtained for the various parameters are shown in Table 3. Despite the presence of sextic correction terms as large as 34 MHz, the majority of the sextic parameters were, at best, poorly determined.

There are too few data available for the $v_5 = 1$ state of HCOF (Table 2) to allow the sextic terms to be included in the fit, and in this case these parameters were constrained at their ground state values. Also the quartic constant D_J had to be fixed to its ground state value due to excessive correlations.

The contribution from sextic terms in the ground state of DCOF is much smaller (< 13 MHz) than in HCOF, and here also the sextic constants are poorly determined. For the lowest vibrational state $v_5 = 1$ of DCOF the same constraints had to be imposed as for this state in HCOF.

As stated above the sextic centrifugal distortion constants are poorly determined. Under these circumstances the values given for these constants in Table 3 have little physical significance, but are nevertheless necessary for the accurate prediction of high-J transitions and reduce the standard errors significantly also for the excited vibrational states. In addition, we believe that the quartic constants are less contaminated with systematic errors than those given in Reference [4].

It is notoriously difficult to make use of centrifugal parameters from the literature (e.g. [9]), because the large number of conventions which may be employed frequently results in confusion and subsequent error. We therefore give in Table 4 the set of Watson's determinable parameters [6, 8] which are more closely related to molecular structure and force fields. These parameters have the advantage of being independent of the representation selected and of the parameters s_{111}, s_{311}, s_{131}, and s_{113} [6]. Since we expect that the constraints imposed in the fitting of the excited states produce systematic errors, in Table 4 the determinable parameters are given only for the ground states. The errors in Table 4 were calculated by error propagation making full use of the variance-covariance matrix.

One might hope that certain linear combinations of otherwise poorly determined parameters can be obtained significantly due to correlation effects. However, inspection of Table 4 shows that this is not true for the sextic constants, and all φ-constants have large uncertainties.

Table 3. Fitted molecular parameters of HCOF and DCOF in MHz[a].

	HCOF, Ground	HCOF, $v_5 = 1$	DCOF, Ground	DCOF, $v_5 = 1$
A	91 156.513 (30)	91 848.213 (93)	65 096.541 (23)	65 379.817 (49)
B	11 760.1507 (45)	11 746.915 (12)	11 761.7594 (50)	11 749.0522 (87)
C	10 396.7610 (39)	10 365.715 (11)	9 941.7422 (38)	9 907.9537 (82)
$D_J \cdot 10^3$	9.739 (24)	9.739[c]	9.050 (28)	9.050[c]
$D_{JK} \cdot 10^3$	– 105.92 (49)	– 106.72 (12)	– 37.01 (44)	– 38.324 (82)
$D_K \cdot 10^3$	3 170.3 (32)	3 316.8 (23)	1 191.4 (15)	1 233.88 (69)
$d_1 \cdot 10^3$	– 1.6773 (15)	– 1.69631 (86)	– 1.9738 (31)	– 1.9999 (21)
$d_2 \cdot 10^3$	– 0.10415 (24)	– 0.11951 (40)	– 0.18350 (65)	– 0.200893 (45)
$H_J \cdot 10^6$	– 0.014 (18)	– 0.014[c]	– 0.028 (48)	– 0.028[c]
$H_{JK} \cdot 10^6$	– 0.49 (70)	– 0.49[c]	– 2.1 (15)	– 2.1[c]
$H_{KJ} \cdot 10^6$	– 43.0 (160)	43.0[c]	16.0 (150)	16.0[c]
$K_K \cdot 10^6$	774.0 (2700)	774.0[c]	100.0 (1200)	100.0[c]
$h_1 \cdot 10^6$	0.0029 (13)	0.0029[c]	0.0009 (70)	0.0009[c]
$h_2 \cdot 10^6$	0.00093 (36)	0.00093[c]	0.0015 (19)	0.0015[c]
$h_3 \cdot 10^6$	0.000163[b] (60)	0.000163[c]	0.00057[b] (29)	0.00057[c]
σ	0.127	0.119	0.131	0.099

[a] The parameters are obtained from Watson's S-reduction using I^r-representation. Errors given in units of last digits, σ is standard error of frequencies.

[b] Calculated from planarity condition for sextic centrifugal distortion constants.

[c] Transferred from ground state.

Table 4. Watson's determinable constants for the ground states of HCOF and DCOF (in MHz). $S = A + B + C$.

	HCOF	DCOF
$\mathfrak{A}$	91 156.532 (30)	65 096.558 (23)
$\mathfrak{B}$	11 760.0605 (49)	11 761.7358 (54)
$\mathfrak{C}$	10 396.6775 (43)	9 941.7265 (42)
τ_{aaaa}	− 12.297 (11)	− 4.6538 (47)
$\tau_{bbbb} \cdot 10^3$	− 53.21 (11)	− 53.46 (13)
$\tau_{cccc} \cdot 10^3$	− 26.372 (88)	− 21.878 (93)
$\tau_1 \cdot 10^3$	309.3 (22)	43.9 (21)
$\tau_2/S \cdot 10^3$	4.56 (28)	− 14.22 (32)
$\varphi_{aaa} \cdot 10^6$	731.0 (2540)	− 87.0 (1060)
$\varphi_{bbb} \cdot 10^6$	− 0.006 (21)	− 0.031 (65)
$\varphi_{ccc} \cdot 10^6$	− 0.018 (16)	− 0.030 (38)
$\varphi_1 \cdot 10^6$	− 133.0 (460)	25.0 (400)
$(\varphi_2 + \varphi_3)/S \cdot 10^6$	0.034 (37)	0.041 (81)
$(\varphi_2 - \varphi_3)/S \cdot 10^6$	− 0.014 (78)	− 0.038 (27)
$\varphi_4/S \cdot 10^6$	− 202.0 (110)	− 24.6 (86)

We also note that the planarity defect for the τ-constants [10]

$$\Delta\tau = (A + B)\,\tau_1 + C\,\tau_{cccc} - \tau_2$$

deviates significantly from zero.

Appendix

Least Squares Fitting with Linear Contraints

A common problem in experimental research is to extract the parameters of interest from experiments measuring these parameters indirectly. Very frequently this is done using the well known (e. g. [11]) method of least squares. In certain applications a slight complication arises from the fact that the desired parameters may or may not depend on additional constraints. An example for this situation is the centrifugal distortion analysis of the rotational spectra of asymmetric top molecules: here additional constraints on the parameters are introduced for planar asymmetric tops by the planarity conditions for the centrifugal distortion constants [8]. For the sake of economy it is desirable to have evaluation programs which handle both cases just by activating an option in the program.

A common procedure in the case of linear equality constraints is to introduce the constraint equations as "observations" with weights large compared to the weights of the experimental observations. However, this procedure has the unfavorable characteristic of increasing the numerical instability and also masks information contained in the experimental result. We therefore have developed a different procedure which does not show these deficiencies.

The procedure can be outlined by consideration of the following problem:

Solve the overdetermined system of linear equations

$$\boldsymbol{U}\boldsymbol{x} = \boldsymbol{r}$$

subject to the NC linear constraint equations

$$\boldsymbol{C}\boldsymbol{x} = \boldsymbol{a}\,,$$

where $\boldsymbol{U}$ is a rectangular $m \times n$ matrix (Jacobian matrix), $\boldsymbol{r}$ is a vector with m elements (experimental measurements or residuals "experimental − theoretical"), $\boldsymbol{x}$ is the vector of the n desired parameters, $\boldsymbol{C}$ is a rectangular $\mathrm{NC} \times n$ matrix (constraint coefficients), and $\boldsymbol{a}$ is a vector with NC elements (right hand side of constraint equations).

This statement of the problem also includes the fitting of nonlinear equations after the proper linearization. Note however, that in the case of nonlinear equations the matrix elements of $\boldsymbol{U}$ and $\boldsymbol{C}$ must vary sufficiently slowly with the parameters $\boldsymbol{x}$ in order to have a convergent iteration.

The problem stated above is solved by the following steps:

1) Construct the augmented overdetermined system of linear equations

   $$\boldsymbol{A}\boldsymbol{x} = \boldsymbol{s}$$

   by adding the matrix $\boldsymbol{C}$ as additional rows to the matrix $\boldsymbol{U}$, and the vector $\boldsymbol{a}$ as additional elements to the vector $\boldsymbol{r}$.
2) Perform NC elimination steps (e. g. [12]) on the augmented matrix $\boldsymbol{A}$ with pivot elements taken exclusively from the part of $\boldsymbol{A}$ originating from the matrix $\boldsymbol{C}$; use maximal pivots.
3) Cut off the augmented part; retain the elements.
4) Solve the resulting system in n-NC unknown parameters by setting up the normal equations or by some other method (orthogonalization, singular value decomposition, etc.).
5) Calculate estimates for variance, standard errors, correlation coefficients, etc.
6) Solve for the parameters eliminated in step 2 by backsubstitution; calculate the standard errors by error propagation using the variance-covariance matrix of step 5.

We have written a subprogram FIT8CS which follows this algorithm. This subprogram is available as FORTRAN IV subroutine. It is also part of our programs ZFAP4 and ZFAP6 for the centrifugal distortion analysis of rotational spectra of planar or nonplanar molecules, which we have used in our work on formyl fluoride.

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